

NASA TTF-12735

PROCESS FOR PRODUCING FLAME RESISTANT POLYURETHANE FOAMS  
GERMAN PATENT 1177816

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N77-14049

Translation of "Verfahren zum Herstellen  
schwerentflammbarer Polyurethanschaumstoffe,"  
German Patent 1177816

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PROCESS FOR PRODUCING FLAME RESISTANT POLYURETHANE FOAMS  
GERMAN PATENT 1177816

Date of Priority 14 February 1963

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ABSTRACT. A process for manufacturing flame resistant polyurethane foams by foaming a mixture of organic diisocyanates in organic compounds with at least two interchangeable hydrogen atoms. A mixture of 10 to 30% by weight of post-chlorinated polyisobutylene with a chlorine content of 35 to 70% by weight and 0.5 to 5% by weight of an organic metal salt complex compound of metals of groups of Ib, Va, VIa, VIIa and VIII of the periodic system of elements (with reference to the total amount of weight of the initial material forming the polyurethane foam) is used as chlorinated polyalkaline and metal salt.

This invention concerns a process for the manufacture of flame resistant polyurethane foams. /1\*

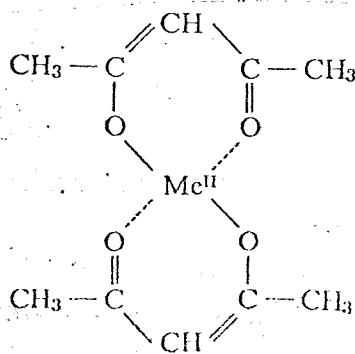
In the polyurethane foams known, additives have been particularly used to provide resistance or increased resistance to fire: unpolymerizable halogen hydrocarbons, such as chloroparaffins or polyvinylchlorides, and also compounds of phosphorus, such as phosphoric acid ester, phosphonic acid ester or phosphinic oxide, and antimony trioxide, antimony acid or adducts of hexahalogen cyclopentadiene and unsaturated aliphatic compounds. The effect of the individual compounds on high resistance to burning can be increased by suitable combinations. However the physical properties of the polyurethane foams can often be unfavorably affected by means of such additions. A further disadvantage is the large amount of additions which are often necessary to make the polyurethane foams flame resistant.

Finally it is known that foams which would be difficult to burn can be produced on the basis of polyurethanes by using high molecular polyvinyl compounds containing chlorine, such as polyvinyl chloride, correspondingly mixed polymers or polychlorostyrene, and compounds of aluminum silicates containing water. As comparison tests between the polyurethanes modified in this manner and the polyurethanes produced in accordance with this invention show, the processes named above require tangibly greater amounts of materials producing flame resistance than does the use of compounds according to this invention.

\*Numbers in the margin indicate foreign pagination.

It was found that polyurethane foams without these disadvantages could be produced by foaming in the usual manner a mixture of organic diisocyanates, organic compounds with at least two interchangeable hydrogen atoms, water and/or other foaming agents, chlorinated polyalkylenes and metal salts, using as chlorinated polyalkylenes and metal salts a mixture consisting of 10 to 30% by weight of post-chlorinated polyisobutylene with a chlorine content of 35-70% by weight, preferably 65-66% by weight, and 0.5-5% by weight, preferably 1.0-2.5% by weight (in correspondence to the total amount of weight of the initial materials producing the polyurethane foam) of an organic metal salt complex compound of metals of groups Ib, Va, VIa, VIIa and VIII of the periodic table of elements, as described in the manual for inorganic and chemical practice by G. Jender and H. Wendt, Seventh edition, p. 470, S. Hirzel-Verlag, Stuttgart, 1949.

Organic complex compounds in the sense of the invention are especially compounds of metals of the above-mentioned groups with diketones, keto carboxylic acids, and their esters, oxyaldehydes or polyketones. For special purposes hydroxy carboxylic acids, keto aldehydes, aldehyde carboxylic acids, hydroxylamino acids and aminophenols can be used. These metal compounds are usually internally complex salts, e.g., they can be represented by an acetylacetonate with the following formula:



In this formula  $Me^{II}$  signifies a bivalent metal from the above-mentioned groups; however, Me can also be univalent, bivalent or polyvalent.

Suitable metal complexes are, e.g., manganese (II)-acetylacetonate, manganese (III)-acetylacetonate, copper (II)-acetylacetonate, iron (III)-acetylacetonate, chromium (III)-acetylacetonate, the lactates of bivalent or trivalent chromium, vanadium, the acetylacetonates of uranium, vanadium, titanium, zirconium, niobium, tantalum, bismuth, tungsten or molybdenum, and the corresponding metal compounds of salicyl-aldehyde or of ethyl acetoacetate.

The metal complexes can be produced by replacing metal salts with the organic chelating agents according to well known methods. These methods are, e.g., described in the works of F. Gauch in Wiener Monatshefte, Vol. 21,

p. 89, 1900, and G. Urbain and A. Debierne in Compt. Rend., Vol. 129, p. 203, 1889, and in Inorganic Synthesis, Vol. 2, p. 10 and Vol. 5, p. 105.

Page One Title

Polyurethane foams produced in this way are particularly difficult to ignite. They are also characterized by the fact that the additives producing and increasing flame resistance have little or no effect upon the other qualities of the polyurethane foams.

The diisocyanates used are those already known to be used in manufacturing polyurethane foams, such as p-phenylene diisocyanate, toluylene diisocyanate, ethylene diisocyanate, hexalene diisocyanate, 4,4'-diphenylene diisocyanate and 1,5-naphthylene diisocyanate.

Suitable and well known organic compounds with at least two active hydrogen atoms are, e.g., the polyesters, i.e., reaction products of polyvalent alcohols and polyvalent carboxylic acids. The expression "polyvalent carboxylic acids" includes acid anhydrides, acid halogenides and the esters of these acids, along with mixtures of these compounds, as well as the acids themselves.

Cover Page Source

It is generally desirable that at least one part of the total polyvalent alcohol used for forming polyesters to be an alcohol with three hydroxyl groups in order to provide sufficient points of application for branching or cross linking. However, the ratio of bivalent alcohol to trivalent alcohol can be selected in accordance with the desired degree of cross linking. These polyvalent alcohols can be aliphatic, cycloaliphatic, heterocyclic or aromatic, saturated or unsaturated. In the molecule of these alcohols different atoms, e.g., oxygen or sulfur, can be inserted between the carbon atoms. These alcohols can also be replaced through the reactions of nondisruptive substitutes, e.g., halogen atoms or ester groups. The following can be mentioned as examples of polyvalent alcohols: glycols, glycerine, polyglycerines, pentaerythritol, polypentaerythritols, mannitol, sorbitol, methyl trimethylol methane, 1,4,6-octane triol, butanediol, pentanediol, hexanediol, dodecanediol, octanediol, chloropentanediol, glycerine monoallyl ether, triethylene glycol, 2-ethyl hexanediol-(1,4), 3,3'-thiodipropandiol, 4,4'-sulfonyl dihexanol, 3,5-dithiohexandiol-(1,6), 3,6-dithiohexandiol (1,8), cyclohexandiol (1,4), 1,2,6-hexanetriol, 1,3,5-hexanetriol, polyallyl alcohol, 1,3-bis-(2-poloxalkol)-propane, 5,5'-dioxydiamyl ether, tetrahydrofuran-2,5-dipropanol, tetrahydrofuran-2,5-dipentanol, 2,5-dioxytetrahydrofuran, tetrahydrothiophene, 2,5-dipropanol, tetrahydropyrrole-2,5-propanol, 3,4-dioxytetrahydropyran, 2,5-dioxy-3,4-dihydro-1,2-pyran, 4,4'-sulfonyldipropanol, 2,2'-bis-(4-oxyphenyl)-propane or 2,2-bis-(4-oxyphenyl)-methane. Open chained, aliphatic, polyvalent alcohols with two to four esterifiable hydroxyl groups and polyalkaline glycols, each with no more than 20 carbon atoms, are preferable.

The polyvalent carboxylic acids used to manufacture the polyesters can be aliphatic, cycloaliphatic, aromatic or heterocyclic, saturated or unsaturated carboxylic acids. The following can be mentioned as examples of polyvalent carboxylic acids: phthalic acid, malic acid, dodecylmalic acid, octadecylmalic acid, fumaric acid, aconitic acid, itaconic acid, 3,3'-thiodipropionic acid, 4,4'-sulfonyldihexanecarboxylic acid, 3-octane-1,7-



conversion. This is the case if the compounds reacting with diisocyanates contain three carboxyl groups when it is water or if compounds are chosen which easily resolve into diisocyanates and easily vaporizable components at high temperatures.

Mixtures of the above mentioned compounds can also be used with one another. The amount used is not critical but depends on the kind of foam desired. To produce very thick foam only a slight amount is needed. To produce a particularly light foam as large an amount should be used as possible. The amount of the compound used in foaming also depends on the type of compound itself.

Although it is not absolutely required, the process according to the invention can be carried out in the presence of well known foam stabilizers in catalysts. Suitable silicone oils and castor oil sulfate are examples.

Dimethyl hexahydroaniline and N-methyl morpholine are examples of catalysts.

The post-chlorinated polyisobutylene of the chelate type used with volatile metal compounds in the sense of the invention can be produced in the usual manner by chlorinating polyisobutylene in tetrachloroethane as a solvent.

It can be used with a chlorine content of 35 to 70, conveniently from 50 to 70, and in amounts where the total chlorine content of the polyurethane foam amounts to between 5 and 25, preferably between 10 and 20.

In order to obtain these qualities the usual adjuvants can be used. Thus fillers such as clay or calcium sulfate, ammonium phosphate, dyes, glass, asbestos and synthetic fibers can be added.

The parts mentioned in the examples are parts by weight.

#### Example 1.

Twenty-three parts of a post-chlorinated polyisobutylene with a chlorine content of 65% are dissolved in 100 parts of a polyester consisting of 5 Mols of adipic acid and 1 Mol of trimethylol propane and 4.5 Mols of ethylene glycol with an OH-number of 60 and a molecular weight of about 2,000. The solution is treated with 2.25 parts of copper (II)-acetyl acetate, 10 parts of water and 40 parts of toluylene diisocyanate and brought to the reaction temperature of 25°C. The reaction product is annealed for 4 hours at 70°C. The foam produced in this way possesses a density of about 50 kg/m<sup>3</sup>, is fine-pored and stops burning 2 to 3 seconds after being taken out of a flame.

#### Comparative Example

In example 1 of the present invention, other things being equal, the following replace the combination producing and/or increasing the flame resistance according to the invention (23 parts of a post-chlorinated

polyisobutylene with a chlorine content of 65% and 2.25 parts of copper (II)-acetyl acetonate):

Page One Title

1. 40 parts of post-chlorinated polyethylene with a chlorine content of 70%. The foam produced in this way does not stop burning outside a flame, but is entirely consumed.

Cover Page Title

2. 20 parts of post-chlorinated polyethylene with a chlorine content of 70%. The foam produced in this way does not stop burning outside a flame, but is entirely consumed.

3. 2.25 parts of copper (II)-acetyl acetonate. The foam produced in this way does not stop burning outside a flame, but is consumed.

4. 23 parts of post-chlorinated polyisobutylene with a chlorine content of 65%. The foam produced in this way does not stop burning outside a flame, but is consumed.

#### Example 2.

Cover Page Source

35.5 parts of a post-chlorinated polyisobutylene with a chlorine content of 65% are dissolved in 100 parts of a polyether made of propylene glycol with an OH-number of 55 and a molecular weight of 1800. The solution is treated with 1.5 parts of iron (III)-acetyl acetonate, 10 parts water and 40 parts toluylene diisocyanate and brought to reaction temperature of 20°C. The reaction product is annealed for 4 hours at 70°. The foam produced in this way possesses a density of 40 kg/m<sup>3</sup>, is fine-pored and stops burning outside a flame in 1 to 2 seconds.

#### Example 3.

If 3 parts of chlorium (III)-acetyl acetonate are used instead of 2.25 parts of copper (II)-acetyl acetonate, and treated as described in Example 1, the result is a foam of density 55 kg/m<sup>3</sup> which is fine-pored and stops burning outside a flame in 1 to 2 seconds.

#### Patent Claim:

A process for manufacturing flame resistant polyurethane foams by foaming a mixture of organic diisocyanates in organic compounds with at least two interchangeable hydrogen atoms such as water and/or other foaming agents, chlorinated polyalkalines and metal salts characterized by the fact that a mixture of 10 to 30% by weight of post-chlorinated polyisobutylene with a chlorine content of 35 to 70% by weight and 0.5 to 5% by weight of an organic metal salt complex compound of metals of groups of Ib, Va, VIa, VIIa and VIII of the periodic system of elements (with reference to the total amount of weight of the initial material forming the polyurethane foam) is used as chlorinated polyalkaline and metal salt.

# REFERENCES

1. USA Patent No. 2,634,244; *Chemisches Zentralblatt*, p. 7054, 1961.
2. USA Patent No. 2,933,462; *British Plastics*, Vol. 34, pp. 541-2, October, 1961.

Cover Page Title

Translated for the National Aeronautics and Space Administration under contract No. NASw-1895 by Techtran Corporation, P.O. Box 729, Glen Burnie, Maryland, 21061.

Cover Page Source

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